

PATENT ABSTRACTS OF JAPAN

(11)Publication number : 09-276708

(43)Date of publication of application : 28.10.1997

(51)Int.Cl.

B01J 35/04

B01D 39/20

B01D 53/94

B01J 21/16

B01J 37/02

F01N 3/10

(21)Application number : 08-091266

(71)Applicant : NIPPON SOKEN INC
DENSO CORP

(22)Date of filing : 12.04.1996

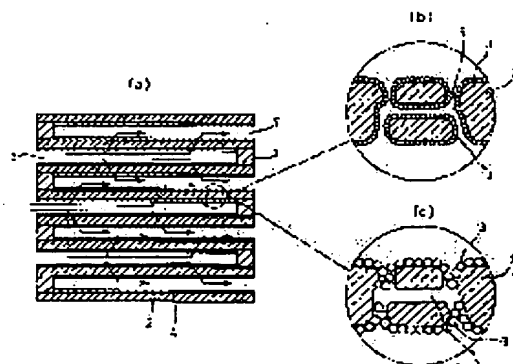
(72)Inventor : NAKAYAMA YOSHINORI
NAKANISHI TOMOHIKO
KAGEYAMA TERUTAKA
KONDO TOSHIHARU

(54) CATALYST FOR CLEANING OF EXHAUST GAS FROM DIESEL ENGINE

(57)Abstract:

PROBLEM TO BE SOLVED: To prevent the coeff. of thermal expansion of a filter from being increased by sealing the openings of the cells of a ceramic honeycomb structure by a specified method, coating the structure capturing particulates only through the side wall with a specified activated alumina slurry and carrying out firing.

SOLUTION: The openings of the cells of a ceramic monolith having a honeycomb structure on the gas inlet 6 side and the gas outlet 7 side are alternately sealed to obtain a filter for purification of exhaust gas from a diesel. The surface of this honeycomb filter made of cordierite and the insides of the pores in the filter are coated with a slurry 3 of activated alumina including $\leq 15\text{wt.}\%$ particles each having $\leq 0.2\mu\text{m}$ particle diameter and then sintering is carried out. The amt. of the slurry penetrating into microcracks in the cordierite crystals is limited, the coeff. of thermal expansion of the resultant catalyst is regulated to $\leq 0.5 \times 10^{-6}/^{\circ}\text{C}$ and coating strength is enhanced.



LEGAL STATUS

[Date of request for examination]

30.05.2002

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

*** NOTICES ***

JPO and NCIPi are not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

CLAIMS

[Claim(s)]

[Claim 1] Exhaust gas in the cell which passes the pore of the cell side attachment wall of a honeycomb, and adjoins by ***** (ing) by turns the both ends of cell opening of the ceramic honeycomb structure object which consists of cordierite A sink, In the porosity ceramic honeycomb filter which was made to carry out uptake only of the particulate contained in diesel exhaust gas a front face and inside the side attachment wall Coating is carried out so that the particle size of 0.2 micrometers or less may coat with the activated-alumina slurry which is an amount not more than 15wt%, may calcinate and may not block the pore of a filter cell side attachment wall among solid-state components. And the diesel emission-gas-purification catalyst characterized by a coefficient of thermal expansion being less than $[0.5 \times 10^{-6} / \text{degree C}]$.

[Claim 2] The diesel emission-gas-purification catalyst which coats with the slurry whose particle size of 0.2 micrometers or less is an amount not more than 10wt% among the solid-state components of an activated-alumina slurry, has coated so that pore of a filter cell side attachment wall may not be blocked by calcinating, and is characterized by a coefficient of thermal expansion being less than $[0.4 \times 10^{-6} / \text{degree C}]$ further in a catalyst according to claim 1.

[Claim 3] The diesel emission-gas-purification catalyst according to claim 1 more than whose 95wt% of the alumina solid-state component in the activated-alumina slurry used for coating is a particle size smaller than the average pore diameter of a porosity ceramic honeycomb filter.

[Claim 4] The diesel emission-gas-purification catalyst whose average pore diameter the porosity after coating an activated alumina in the catalyst of claim 1 is 5 micrometers or more 35 micrometers or less at 40% or more.

[Translation done.]

*** NOTICES ***

JPO and NCIPi are not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention removes a particulate at least among the matter contained in the gas discharged by internal combustion engines, such as a diesel power plant, and relates to the filter for particulate uptake used in order to purify exhaust gas.

[0002]

[Description of the Prior Art] The matter harmful to the body is contained in the particulate discharged by internal combustion engines, such as a diesel power plant, and it has been a technical problem on an environment to remove this. For this reason, in the former, after it carries out uptake of the particulate and it carries out constant-rate uptake with the filter prepared in the exhaust air system of a diesel power plant, the approach of carrying out combustion removal of the particulate by the electric heater, a burner, etc. is performed. Moreover, the combustion temperature of a particulate [the platinum metal catalyst supported in the filter] is lowered, and there is also a method of burning continuously the particulate which carried out uptake. In the case of the approach of carrying out combustion removal of the particulate in which the former carried out uptake by the electric heater, a burner, etc., the filter maximum temperature at the time of combustion rises, a filter may be damaged with the thermal stress concerning a filter, and, for this reason, the particulate amount control of uptake is so important that there are many particulate amounts of uptake, but it is difficult to control the amount of uptake completely. Since the thermal stress which combustion temperature becomes comparatively low and is applied to a filter becomes small in combustion by the latter catalyst, it excels in thermal resistance.

[0003] Generally in the above-mentioned approach, the cordierite which shows low-thermal expansibility is mainly used for particulate uptake as the quality of the material, using the honeycomb structure object of a ceramic in many cases.

[0004] For example, the diesel emission-gas-purification filter of this invention ***** cel opening of one end of the ceramic monolith of honeycomb structure, cel opening by the side of a gas inlet is ***** (ed) every piece, and cel opening by the side of a gas outlet is chisel ***** (ed) about the cel which opening of an entrance side is not ***** (ing). Therefore, a gas component passes the pore of a cel side attachment wall among exhaust gas, and uptake of the particulate which is the solid-state component of exhaust gas is carried out inside the front face of this cel side attachment wall, and the pore of a cel side attachment wall.

[0005]

[Problem(s) to be Solved by the Invention] When supporting metal catalysts, such as platinum, in the above diesel emission-gas-purification filters, in order to distribute a metal catalyst, it is required to carry out coating of the high specific-surface-area ingredient to the interior of the front face of a filter and filter pore as catalyst support beforehand. (Or a filter may be made to carry out coating of the metal catalyst to a high specific-surface-area ingredient and coincidence) Especially, an activated alumina is suitably used as a high specific-surface-area ingredient. (The cordierite currently used for a filter material does not almost have specific surface area.)

[0006] Although high specific-surface-area ingredients, such as the conventional activated alumina, generally use a binder for the improvement in coating on the strength, as a binder, alumina sol, a silica sol, an aluminium nitrate, etc. are desirable. (It may not limit to these three kinds of especially binders, and a with a particle size of less than 0.2 alumina (an activated alumina is included) is sufficient.) Compared with the particle size of an activated alumina, the sufficiently small alumina particle or the silica particle is contained in these binders (about 0.1 micrometers or less), and an activated alumina and the binder of the cordierite of a filter material are committed. Moreover, these binders have the work which raises the

dispersibility of a slurry, and the homogeneity of coating. However, if the nature filter of cordierite is coated by the slurry which mixed these, the problem that the coefficient of thermal expansion of a filter increases sharply may arise. The increment in a coefficient of thermal expansion is so high that there are many rates that what has a fine particle size occupies especially in a slurry.

[0007] The cordierite used as a filter material can attain the very low coefficient of thermal expansion not more than $0.2 \times 10^{-6}/\text{degree C}$ by controlling a presentation and baking conditions. In addition to the cordierite crystal itself and low-temperature expansibility being shown, the low-temperature expansibility of cordierite originates in the coefficient of thermal expansion of the direction of a knockout of a honeycomb becoming small especially by the orientation of the cordierite crystal by extrusion molding. Further very low thermal-expansion nature is attained by absorbing the thermal expansion of a cordierite crystal in a baking process by the micro crack generated into a cordierite crystal. Therefore, a lower coefficient of thermal expansion is obtained, so that there are many micro cracks. However, since the thermal-expansion absorption function of a micro crack is spoiled by entering the clearance between micro cracks since particle size is small, a coefficient of thermal expansion increases the alumina sol coated with the slurry containing an activated alumina and said binder.

[0008] A presentation is the range SiO_2 which can do many cordierite crystals by baking, i.e., near a cordierite theoretical presentation value. : aluminum 2O_3 : $\text{MgO} = 50.3:35.9:13.8$ (wt%) is the most suitable, and since $\text{SiO}_2 = 49.8$ to 50.8 , aluminum $2\text{O}_3 = 35.4$ - 36.4 , and crystal phases' other than a cordierite crystal (for example, a mullite, a spinel, etc.) $\text{MgO} = 13.3$ - 14.3 decrease, a coefficient of thermal expansion becomes low.

[0009] Moreover, h is [that the honeycomb mold filter fabricated by extrusion should just be the programming rate which does not break in contraction by sintering / maximum temperature / a room temperature to] desirable [baking conditions] in 5 degrees C/h - 150 degrees C /. The maximum-temperature range has 1420 degrees C - desirable 1440 degrees C, and it is 1425 degrees C - 1435 degrees C most preferably. The temperature lower several degrees C than the temperature which cordierite fuses of especially a maximum temperature is the optimal. Since the holding time of a maximum temperature calcinates at temperature uniform to the interior of a filter, 5 hours - 20 hours are desirable.

[0010] In this way, since the sintered nature honeycomb filter of cordierite prepared the presentation to the cordierite theoretical presentation, there are few phases other than cordierites, such as a spinel and a mullite, it controls baking conditions, and is generating many micro cracks during a cordierite crystal. Therefore, a coefficient of thermal expansion serves as less than [$0.2 \times 10^{-6}/\text{degree C}$] and a very low value.

[0011] The die length of the width of face of the micro crack generated during a cordierite crystal in a baking process is several micrometers - dozens of micrometers in about 0.05 micrometers - about 0.2 micrometers. If the particle size of an activated-alumina slurry is 0.2 micrometers or less, it will infiltrate into the clearance between micro cracks, the thermal-expansion absorber style by the micro crack will be destroyed, and the coefficient of thermal expansion of cordierite will be increased sharply.

[0012]

[Means for Solving the Problem] The diesel emission-gas-purification catalyst of this invention is characterized by the increment in a coefficient of thermal expansion be small, even if the particle size of 0.2 micrometers or less maintains the thermal-expansion absorber style of a micro crack with restrict the amount of less than [of total weight / $10\text{wt}\%$], and the activated-alumina slurry which coats with the activated-alumina slurry not more than $5\text{wt}\%$ more preferably, and infiltrates into the micro crack under cordierite crystal and coats the interior of the front face of the honeycomb mold filter of the cordierite quality of the material, and pore with an activated alumina. A kind of platinum groups, such as platinum, have a desirable metal catalyst furthermore supported at least inside a filter front face and pore. As for the catalyst of this invention, it is possible after activated-alumina coating for it to be a coefficient of thermal expansion not more than $0.5 \times 10^{-6}/\text{degree C}$. Furthermore, it is desirable that it is less than [$0.4 \times 10^{-6}/\text{degree C}$].

[0013] The porosity of the filter after coating a honeycomb mold filter with high specific-surface-area ingredients, such as an activated alumina, by the coating approach of this invention is suitable for using it as a diesel particulate filter 40% or more, since a pressure loss is low and collection efficiency is high if an average pore diameter is 5 micrometers or more 35 micrometers or less and is 10 micrometers - 30 micrometers preferably at 65% or less.

[0014] The cel of an outlet side is discharged from the outlet of a cel where the gas which flowed from the cel of an entrance side as structure for the diesel emission-gas-purification filter of this invention to carry out uptake of the particulate contained in the exhaust gas of a diesel power plant passes through a cel side attachment wall for a **** suggestion ***** reason, and adjoins. When passing through a cell wall,

uptake only of the particulate in exhaust gas is carried out. At this time, when the porosity and average pole diameter of a filter are smaller than the aforementioned range, particulate collection efficiency improves, but since the pressure loss of a filter becomes high and engine power declines, it is not desirable. Moreover, since particulate collection efficiency will fall if an average pole diameter is larger than this range, and the mechanical strength of a filter will be reduced if porosity is larger than this range, it is not desirable.

[0015] Although it is most desirable that it is a particle size smaller than the average pole diameter of a filter as for the particle size of the activated alumina with which a filter is coated on the other hand, it is [more than 95wt% at least] desirable to use a particle size of an activated alumina smaller than the average pole diameter of a filter. When activated-alumina particle size is larger than the average pole diameter of a filter, since do not go into the pore inside the cel side attachment wall of a filter, but a wrap activated alumina increases a cel side-attachment-wall front face relatively, the thickness of a coating layer becomes thick and a pressure drop buildup becomes large, an activated alumina is not desirable. Moreover, when activated-alumina particle size is smaller than the average pole diameter of a filter, the activated aluminas included in the pore inside a cel side attachment wall increase in number. The rise of a pressure loss can be suppressed by distributing homogeneity and coating, without performing the Ayr blow or suction with a cleaner enough at this time, removing an excessive activated-alumina slurry, and making the inside of pore blockade. Moreover, among particle size with an activated-alumina particle size smaller than the average pole diameter of a filter, as for a thing 0.2 micrometers or less, less than [of activated-alumina slurry all weight / 10wt%] is desirable by the above-mentioned reason, and it is less than [5wt%] more preferably.

[0016] The reason the particle diameter of high specific-surface-area ingredients, such as an activated alumina, is the above range is because a high specific-surface-area ingredient needs to trespass upon the interior of the pore of the cel side attachment wall of a filter. Although only the front face of a cel side attachment wall coated honeycomb mold monolith support with the high specific-surface-area ingredient conventionally, since the particulate contained in exhaust gas stops on the front face of the cel side attachment wall of a filter, and at the interior of the pore of a cel side attachment wall in the case of the honeycomb mold filter of the structure where exhaust gas passes through the interior of pore of a cel side attachment wall, a particulate needs to contact inside this high specific-surface-area ingredient and pore at this time in order to receive a catalysis. Therefore, the aforementioned particle size is required for a high specific-surface-area ingredient.

[0017] The diesel emission-gas-purification filter of this invention carries out uptake of the particulate contained in the exhaust gas of a diesel power plant at least, and carries out combustion removal. A filter is coated with high specific-surface-area matter, such as an activated alumina, for making a platinum group catalyst metal into the support for carrying out coating. Generally, a platinum group catalyst metal is used as a catalyst which lowers a particulate combustion temperature, and is further used as an oxidation catalyst of a carbon monoxide or a hydrocarbon. The filter of this invention is a diesel emission-gas-purification filter which has supported the metal catalyst which consists of at least one kind of platinum group metals.

[0018] Next, the diesel emission-gas-purification filter of this invention is concretely explained with drawing 1 . Like drawing 1 a, the porosity ceramic filter of this honeycomb structure forms the coating layer 4 which becomes the cel side attachment wall 2 of a honeycomb mold filter from the activated-alumina particle 3 by ***** (ing) the both ends of a monolith honeycomb by turns by the ***** material 1. If the activated alumina of a particle size smaller than the average pole diameter of a filter is used like drawing 1 b, since coating is carried out without blockading the interior of the pore 5 of a cel side attachment wall, there are few pressure drop buildups of a filter. However, since the pore of a cell wall is made to blockade when the activated alumina of a bigger particle size than the average pole diameter of a filter is used like drawing 1 c, the pressure loss of a filter goes up sharply. Moreover, the purification effectiveness of the exhaust gas components (HC, CO, etc.) of a particulate and others by which uptake was carried out to the coating part of an activated alumina inside the cell wall by supporting a platinum group catalyst metal is raised.

[0019] The diesel exhaust gas containing a particulate advances into a cel from the cel entrance side 6, passes a cell wall 2, and leaves it from the cel outlet side 7. At this time, uptake of the particulate is carried out by the pore of a cell wall front face and the interior. Although a platinum group catalyst metal is anew coated after it coats an activated alumina, it is also possible to coat with the solution mixed with the activated alumina.

[0020] When an activated-alumina slurry infiltrates into the clearance between the micro cracks 9 which exist during the cordierite crystal 8, a coefficient of thermal expansion increases (drawing 2). In this invention, by specifying the range of the particle size of the activated-alumina slurry used for coating, the

activated-alumina slurry which infiltrates into a micro crack is restricted, and the increment in the coefficient of thermal expansion of the filter by coating is controlled.

[0021] The filter coated using the above ingredients can be suitably used as a diesel particulate filter of low voltage loss. Below, the example and example of a comparison are shown.

[0022]

[Example] A silica, an aluminum hydroxide, and talc are used for the main raw material (the presentation of a raw material is Table 4). It adds. the carbon (mean particle diameter of 50 micrometers) for adjusting so that it may become a cordierite (2MgO , $2\text{aluminum}_2\text{O}_3$, and 5SiO_2) presentation, and then making it porosity -- these main raw materials -- receiving -- $20\text{wt}(\text{s})\%$ -- Produce a ceramic honeycomb structure object by the well-known extrusion process, and it calcinates by the holding time of about 10 hours by the maximum temperature of about 1420 degrees C - about 1430 degrees C, the programming rate of about 5 degrees C - about 150 degrees C, and the maximum temperature. Porosity had the pore property which is the average pole diameter of about 30 micrometers about 55%, and 12 porosity cordierite honeycomb structure objects with a diameter [of about 140mm] and a die length of about 130mm about 0.45mm in cel side-attachment-wall thickness and whose numbers of cels per 1 square inch are about 150 pieces were acquired.

[0023] On the other hand, in the solution which mixed 670g of activated aluminas of 5 micrometers of diameters of a centriole (drawing 3) with 4l. of water as a high specific-surface-area ingredient Six levels of coat liquid to which the amount of the alumina sol (the product made from the Nissan chemistry and aluminum 2O_3 content about 10 wt(s)%) to add was changed with 0g, 170g, 330g, 670g, 1000, 1330g, and 1670g were produced (coat liquid A, B, C, D, E, F, and G).

[0024] It dips completely the two aforementioned porosity cordierite honeycomb structure objects at a time in the activated-alumina slurry of A-F, respectively (wash coat). Then, the slurry which adhered too much in an air cleaner and compression Ayr is removed as completely as possible. It produced each a total of two activated-alumina coating honeycombs [12] coated with six kinds of slurries of A-F which repeated coating and made the amount of coats about 65 g/L (A-1, A-2, B-1, --, G-1, G-2). Furthermore, it dried at about 120 degrees C for about 2 hours, and after that [each] was calcinated at about 800 degrees C. The amount of coats per unit volume was computed from the honeycomb weight difference before and behind a wash coat <amount of coats [g/L]=(after [a before / a coat / weight-coat] weight)/(honeycomb volume)>. Rates, such as the amount of coats and loadings of each slurry, and particle size, are shown in Table 1. Then, after dipping 0.1 mols of each into the chloroplatinic acid water solution of /L for about 30 minutes and making it dry at about 120 degrees C for about 2 hours, it calcinated at about 800 degrees C, and platinum was made to support. All the ten amounts of support of platinum were about 2 g/L.

[0025] Mol opening by the side of the gas inlet of the honeycomb structure object which carried out wash coat processing is ***** (ed) every piece, and it ***** [chisel] in a gas outlet side about the cel which is not ***** (ing) by the entrance side. Especially as long as ***** material is a ceramic ingredient with the thermal resistance of 1000 degrees C or more, such as cordierite, an alumina, and a zirconia, it may not be limited, but the adhesives made from a ceramic are sufficient as it. Thus, the diesel emission-gas-purification catalyst was produced (Support A - support G).

[0026] The filter produced the sample cut into the magnitude of $\phi 5\text{ mm} \times \text{L}20\text{mm}$, and measured the coefficient of thermal expansion. A result is shown in Table 3. Moreover, the cold energy cycle trial was performed for the sample cut into the magnitude of $\phi 15\text{ mm} \times \text{L}10\text{mm}$ from the filter, and the exfoliation rate of an activated alumina was investigated. The result is shown in Table 2. An activated-alumina exfoliation rate is a formula. - It asked by (1).

[Equation 1]

活性アルミナ剥離量 (g) = 試験前重量 - 試験後重量

$$\text{活性アルミナ剥離割合 (wt\%)} = \frac{\text{活性アルミナ剥離量 (g)}}{\text{活性アルミナコート量 (g)}} \times 100(\%) \text{ 式- (1)}$$

[0027] Although a coefficient of thermal expansion becomes small so that there is less particle size of 0.2 micrometers or less among the solid-state components of an activated-alumina slurry than a coefficient-of-thermal-expansion result, on the other hand, the amount of exfoliations increases (drawing 4). From these results, if the particle size of 0.2 micrometers or less carries out a wash coat among the solid-state components of an activated-alumina slurry by less than [more than $2.5\text{wt}\%$ $15\text{wt}\%$] and the gamma alumina slurry which is less than [more than $2.5\text{wt}\%$ $10\text{wt}\%$] more preferably, the coating reinforcement of gamma alumina is high at a low-fever expansion coefficient, and it is suitable for the diesel emission-gas-purification catalyst.

[0028]
[Table 1]

表 1

	(wt%)								
	SiO ₂	MgO	Al ₂ O ₃	Fe ₂ O ₃	TiO ₂	CaO	Na ₂ O	K ₂ O	IgLoss
タルク	62.3	31.4	0.30	0.55	0.01	0.20	0.01	0.01	5.20
シリカ	99.9	*	*	*	*	*	*	*	*
水酸化アルミニウム	0.01	*	99.7	0.01	*	*	0.30	*	*

(*は未検出)

[0029]
[Table 2]

表 2

活性アルミナスラリーの配合量及び粒径

	スラリー A	スラリー B	スラリー C	スラリー D	スラリー E	スラリー F	スラリー G
水* (cc)	4000	4000	4000	4000	4000	4000	4000
活性アルミナ(g)	670	670	670	670	670	670	670
アルミナゾル(g) (アルミナゾル中のAl ₂ O ₃ 量(g))	0 (0)	170 (17)	330 (33)	670 (67)	1000 (100)	1330 (133)	1670 (167)
粒径0.2 μm以下の活性アル ミナスラリーの割合 (wt%)	1.5	3.8	6.6	10.0	14.2	17.6	21.1
粒径30 μm以上の活性アル ミナスラリーの割合 (wt%)	5未満	5未満	5未満	5未満	5未満	5未満	5未満

* イオン交換水

[0030]
[Table 3]

表 3

	平均 細孔径 (μm)	気孔率 (%)	活性アル ミナコー ト量 (g/L)	スラリー中の固 体成分のうち粒 径0.2 μm以下 の割合 (wt%)	熱膨張係数 (×10 ⁻³ /℃)			活性アル ミナ 剥離割 合(%)	備 考
					コート前 (①)	コート後 (②)	増 加 量 (②-①)		
担体A-1	30	53	67	1.5	0.11	0.14	0.03	7.2	比較例
担体A-2	28	58	60	1.5	0.09	0.18	0.09	7.0	比較例
担体B-1	27	55	63	3.8	0.18	0.26	0.08	4.5	比較例
担体B-2	33	59	59	3.8	0.11	0.17	0.06	4.3	比較例
担体C-1	29	60	60	6.6	0.13	0.29	0.16	3.5	本発明
担体C-2	28	55	71	6.6	0.15	0.33	0.18	3.4	本発明
担体D-1	29	52	67	10.0	0.10	0.35	0.25	2.7	本発明
担体D-2	30	49	71	10.0	0.12	0.35	0.23	2.4	本発明
担体E-1	28	55	66	14.2	0.14	0.40	0.26	2.0	本発明
担体E-2	31	54	65	14.2	0.09	0.39	0.30	2.1	本発明
担体F-1	33	56	66	17.6	0.13	0.44	0.31	1.8	比較例
担体F-2	31	55	64	17.6	0.18	0.45	0.27	2.3	比較例
担体G-1	30	55	60	21.1	0.20	0.55	0.35	1.8	比較例
担体G-2	29	54	62	21.1	0.15	0.56	0.41	1.7	比較例

[Translation done.]

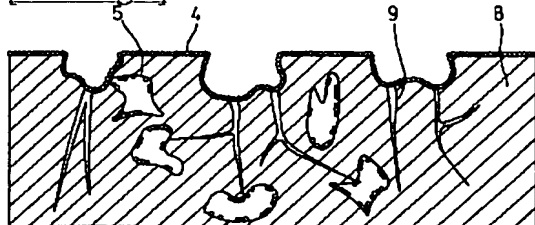
* NOTICES *

JPO and NCIP are not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

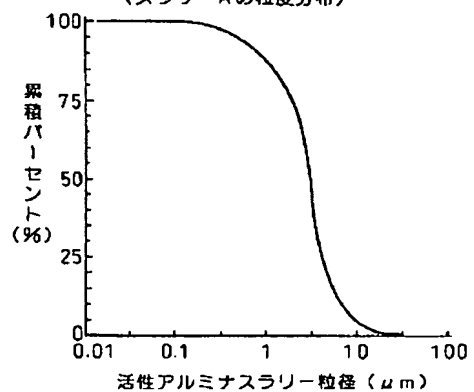
DRAWINGS

[Drawing 2]

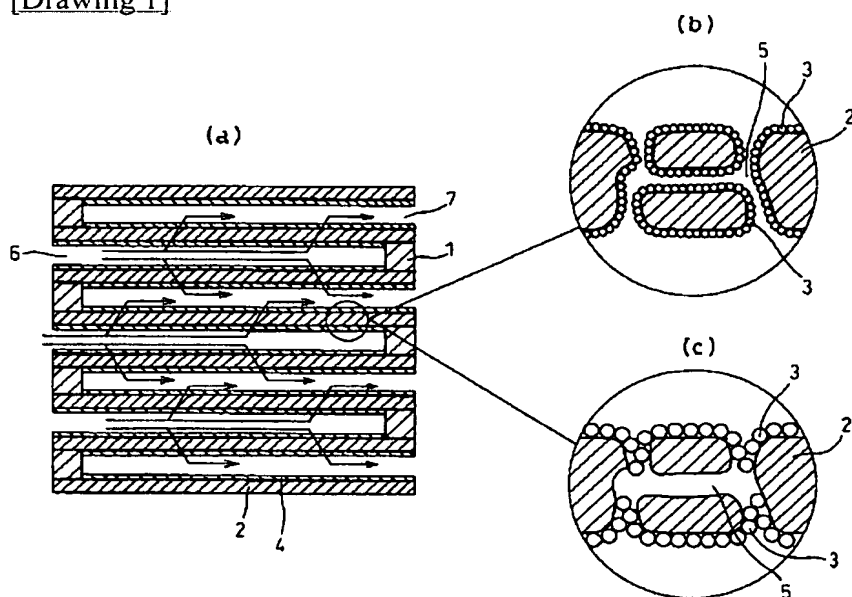


[Drawing 3]

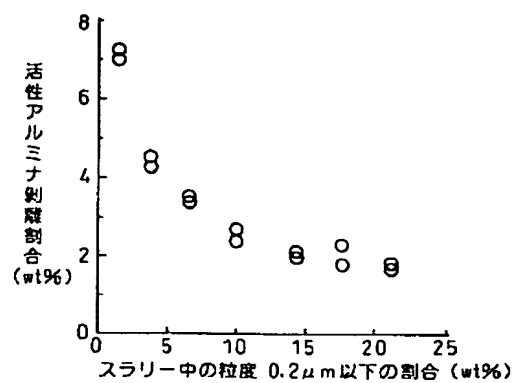
(スラリー A の粒度分布)



[Drawing 1]



[Drawing 4]



[Translation done.]